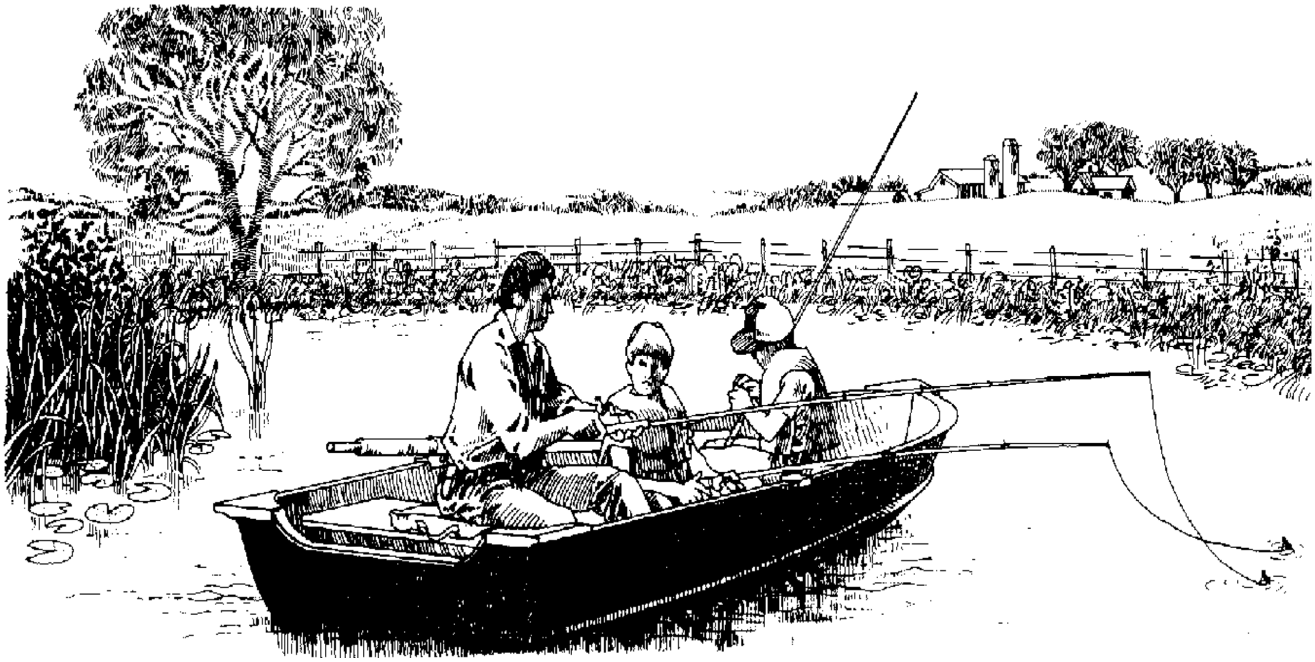
Bass Lake Alum Evaluation Project - Final Report

February 2023



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Introduction & Project Setting

Bass Lake is a 37.4 acre hard water drainage lake located in southwest Marinette County, Wisconsin (T31N, R20E, S28). The Lake has a maximum depth of 62 feet, and an average depth of 23 ft. Most of the lakeshore is low-lying and dominated by northern white cedar (*Thuja occindentalis*). The lake has a small improved boat landing on the west shore that is owned by the Town of Beaver. Four private dwellings area located on the shoreline.

The 451 acre watershed consists of 83% cropland and one active dairy farm housing approximately 1300 animal units. The lake also receives drainage from a 3.4 acre unnamed spring lake, a spring-fed farm pond and several spring seeps located on the north shore of the lake (Figure 1).

Bass Lake has a long history of water quality problems caused by animal waste runoff from unconfined manure stacks and animal feedlots. In the mid 1960's, the lake supported a diverse sport fishery and was popular with local anglers. The fish population included largemouth bass, northern pike, and panfish. The Wisconsin Department of Natural Resources (WDNR) also stocked trout in Bass Lake for several years. Trout stocking was suspended in 1975 after hypolimnetic oxygen concentrations declined and the lake could no longer support a coldwater fishery. Subsequent winter fish kills decimated the lake's warm water fishery as well.

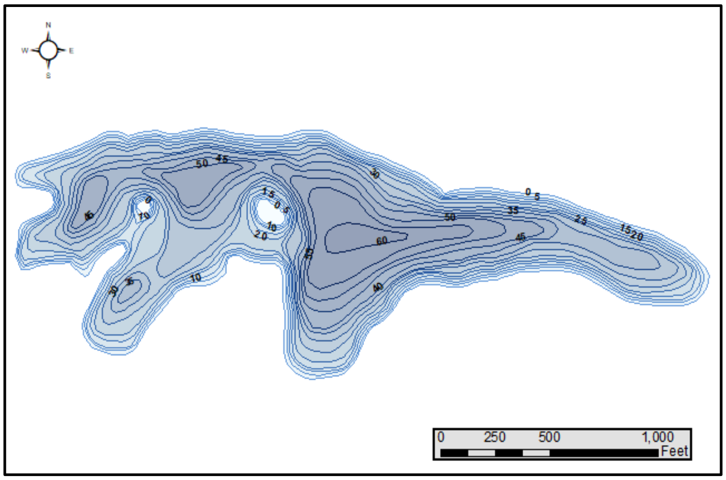

Figure 2. Bass Lake morphometry.

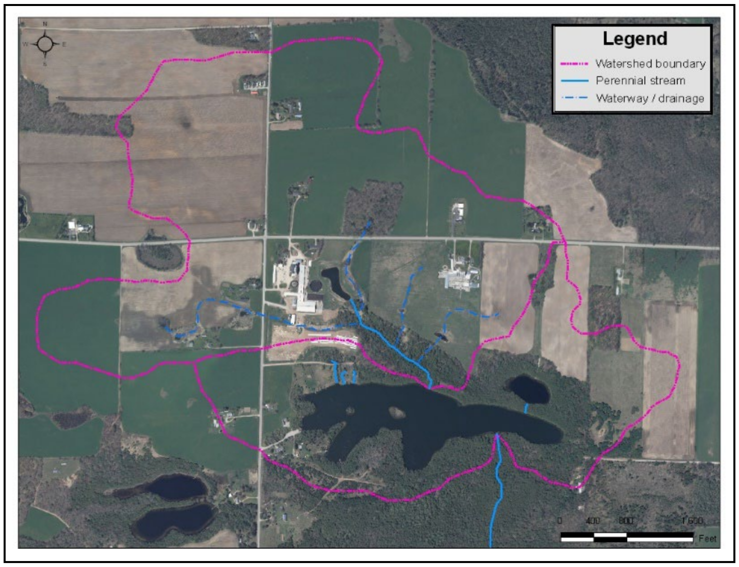

Figure 1. Agriculture is the dominant land use in the Bass Lake watershed.

In 1986 the Wisconsin DNR and Marinette County Land & Water Conservation Division (LWCD) published "A Plan for the Control of Nonpoint Sources in the Bass Lake Watershed" to reduce animal waste runoff to Bass Lake and restore the lakes water quality. After more than 10 years of runoff pollution control efforts, an alum treatment was conducted on Bass Lake in 1999 to reduce internal phosphorus loading. This report details those efforts and tracks the fate of Bass Lake in the 23 years since the alum treatment.

Lake Morphometry & Water Quality

The Bass Lake basin is deep with steep sides (Figure 2) and approximately 60% of the lake volume lies below the thermocline (Figure 3). The lake also has a small surface area relative to mean depth (stratification factor = 42.7), and is sheltered from the prevailing winds. These factors result in strong thermal stratification that resists mixing during spring and fall turnover. Water quality monitoring shows that the lake is weakly meromictic, with prolonged periods, often several years in length, where the lake will fail to mix uniformly.

Strong thermal stratification, and incomplete and unpredictable nature of mixing events, results in

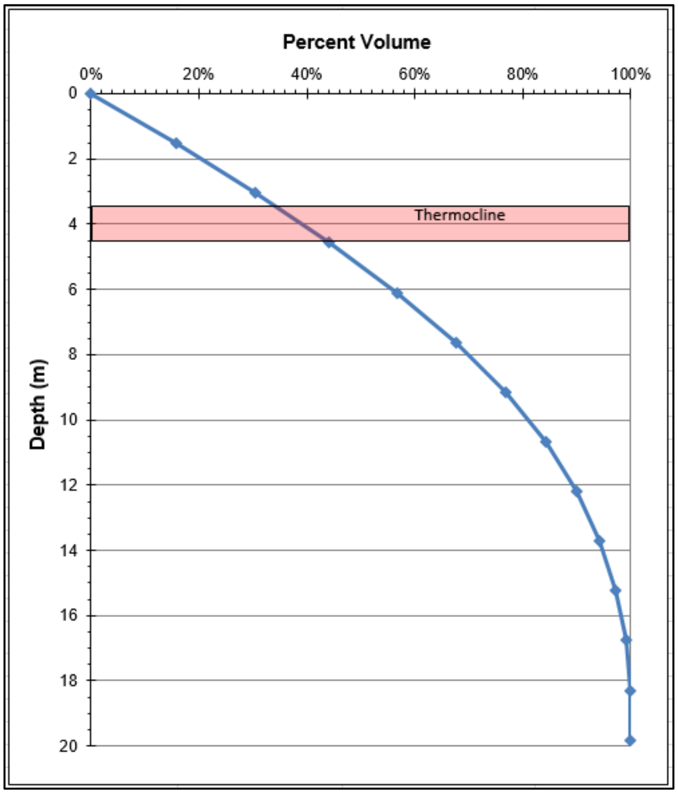

Figure 3. A hypsographic curve for Bass Lake shows more than 60% of the lake volume below the thermocline.

wildly varying surface total phosphorus concentrations (Figure 4). During periods where mixing is limited, surface water quality can be excellent, with low phosphorus levels and good water clarity. These "clear-water" periods are interrupted by hypereutrophic conditions characterized by toxic blue-green algae blooms and fish kills. In one example, during the three-year period between spring of 1996 and fall of 1998, surface total P levels never exceeded 33ug/l. However, during this period hypolimnetic P levels climbed to 1,740 ug/l. When the lake finally mixed well in the fall of 1998, surface total P increased to 872 ug/l. The mass of hydrogen sulfide released from the hypolimnion could be smelled more than a mile downwind of the lake and the resulting oxygen depletion caused a rare open-water fish kill.

History of Nonpoint Source Pollution Control Efforts

Bass Lake was selected as a small-scale priority watershed project under the Wisconsin DNR Nonpoint Source Pollution Control Program in 1984. The goal of the project was to reduce runoff pollution to Bass Lake from agricultural sources. Both farm operators in the watershed cooperated fully and installed the recommended best management practices (BMP's) to reduce runoff pollution. These practices included clean water diversions, roof runoff management, and concrete feedlots with filter strips at both farms. Both farms also installed manure storage facilities to eliminate winter-spread manure and facilitate proper nutrient management. Despite these efforts, water quality conditions continued to deteriorate and the lake was plagued by severe algae blooms and periodic fish kills.

By 1994 State and local resource agencies believed that watershed P loading had been adequately controlled and that internal loading alone was responsible for the continuing poor water quality in Bass Lake. In an effort to complete the restoration the Marinette County Land & Water Conservation Division (LWCD) received a Wisconsin DNR Lake Protection Grant to inactivate phosphorus laden

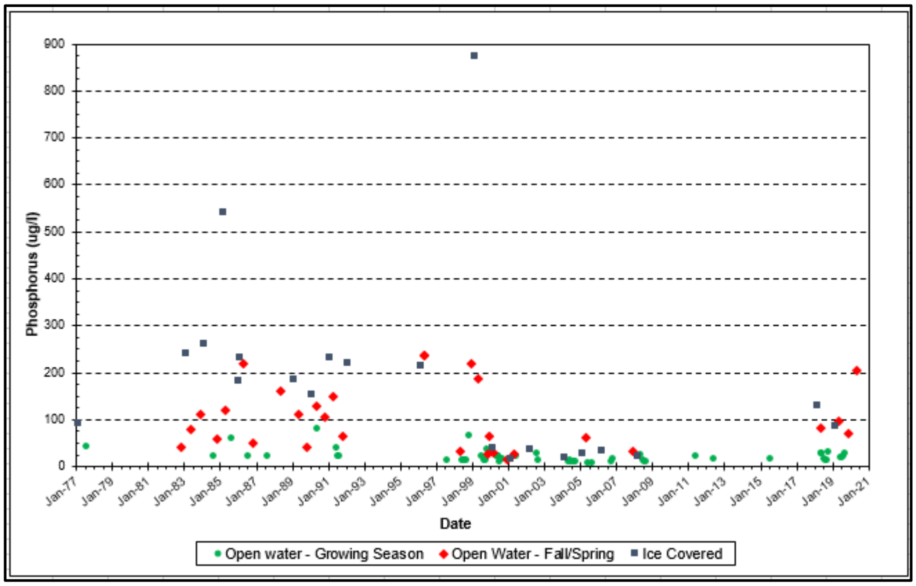

Figure 4. Surface total P varies greatly depending on the frequency and "completeness" of mixing events.

Figure 5. Alum was applied to Bass Lake in November 1999

bottom sediment with alum. The alum treatment was originally scheduled for July 1996. However, further water quality monitoring showed that total P concentrations in the lake inlet were still excessive (2,560 ug/l) during a heavy rain event with even higher P levels in runoff collected below the engineered filter strips (> 16,000 ug/l). Subsequent monitoring of runoff from the spring-fed farm pond also showed greatly elevated P levels. In hindsight it was clear that, given the proximate location to the lake, and the ongoing changes in dairy herd management, many of the old BMP's were not the best alternatives for P removal.

In 1998 the LWCD received a WDNR Targeted Runoff Management (TRM) Grant to pursue permanent "abandonment" of one watershed farm. All cattle were remove from the site and Wisconsin Stewardship Program funds were utilized to purchase a conservation easement on more than 55 acres of cropland and almost 2000 feet of Bass Lake's shoreline. On the second farm, the outdoor feedlot was abandoned and animals were moved into a freestall facility. A second liquid manure storage facility was also constructed and enriched sediment was dredged from the spring-fed farm pond. Together, these changes eliminated direct animal waste runoff from farms in the Bass Lake watershed.

Pre-Alum Phosphorus Load Modelling

In 1998 the FLUX$_{32}$ Mass Transport Program developed by the US Army Corps of Engineers was used to model nutrient loading to Bass Lake based on 1997-98 stream discharge and phosphorus concentration data. Stream discharge to Bass Lake was measured with a continuous water level recorder installed above a small V-notched weir installed approximately 150 feet upstream from the lake. Grab samples were collected from the stream throughout the monitoring period at various flows. The loading model predicted a P load of approximately 75 kg during the open water season. It was estimated that 15 kg/yr could be attributed to base flow with the balance coming from runoff events.

Using the Wisconsin Lake Model Spreadsheet (WILMS) it was estimated that Bass Lake would be able to assimilate the base P load and still maintain acceptable water quality if internal loading could be addressed and runoff event loads could be drastically reduced. Assuming runoff event loading could be controlled the WILMS model predicted a post-alum treatment spring turnover phosphorus concentration of 12 - 24ug/l. Long term monitoring also suggested the lake would be able to assimilate the elevated base flow loading without an appreciable decrease in water quality. Bass lake is a hard water lake and marl formation appears to remove a significant amount of phosphorus from surface waters.

Alum Application

With the new phosphorus controls in place, and promising results from water quality modeling, the Bass Lake alum treatment was completed on November 3, 1999. The contractor applied 61,475 gallons of alum to the surface of Bass Lake during a two-day period. Weather conditions were favorable and the entire process was completed without complication (Figure 5). The original grant project called for applying approximately 12,000 gallons of alum to Bass Lake for an in-lake concentration of 2.1 mg/l of Al^{+3}. However, after studying the success of past alum treatments and consulting a variety of lake management experts it was decided that increasing the dosage to maximize phosphorus control at the sediment water interface would improve the chances for long-term success (Rydin

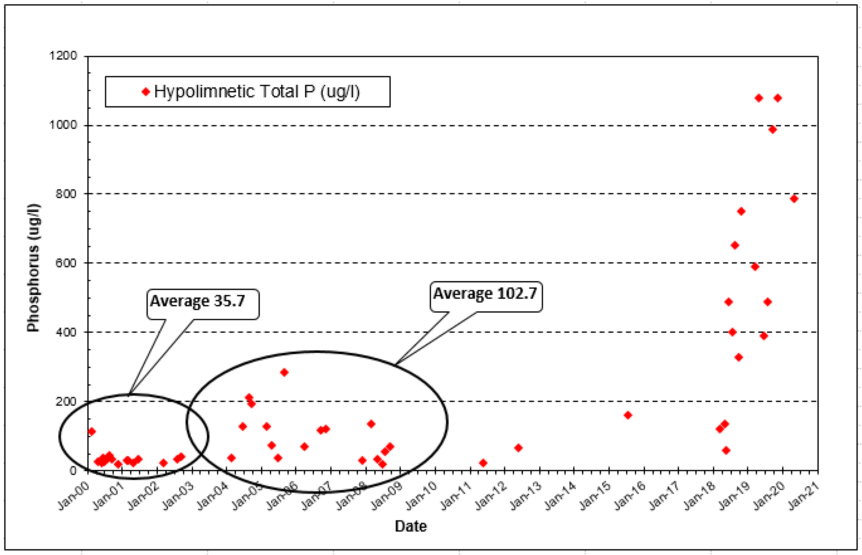

Figure 6. Hypolimnetic total-P concentrations were greatly reduced following the alum application.

and Welch 1998), (Kennedy and Cooke 1982). A titration of lake water with liquid alum revealed that the lake had the buffering capacity to assimilate a dose of 21.9 mg/l of Al^{+3}. In the end, the grant budget was increased to allow for an alum dose of 61,000 gallons, resulting in an in-lake concentration of 10mg/l of Al^{+3}, far below the maximum safe dose. On an aerial basis $91 g/m^2$ of Al^{+3} was deposited on the sediment surface, more than twice the level of other successful alum treatments in Wisconsin lakes.

Post-Alum Application Water Quality

At the time of the 1999 alum application, Bass Lake was still stratified with a hypolimnetic total P concentration of 1,120 ug/l and a surface total P concentration of 36 ug/l. As the aluminum floc settled to the lake bottom, hypolimnetic total P levels declined precipitously, measuring only 26 ug/l by the spring of 2000 (Figure 6). In the three years after the alum treatment, hypolimnetic total P averaged 35.7 ug/l despite complete anoxia during the summer and winter months.

In 2008 a follow-up study was conducted to evaluate post-treatment water quality data and model nutrient loading in light of changes in farm operations in the Bass Lake watershed. The average hypolimnetic total P concentration for the period from 2004 through 2008 was 102.7 ug/l (Figure 6). While the increase in hypolimnetic phosphorus was significant, it did not translate into declining water quality, as the average surface total P concentration during the same period was 17.7 ug/l.

Stream discharge to Bass Lake was monitored in 2008 using a water level recorder and a re-built V-notch weir. A comparison of flow records for 1997/98 and 2008 shows that the seasonal trend was roughly the same but 2008 lacked the intense summer rain events and associated high flows. During both monitoring periods "base flow" representing spring seeps, wetland discharge and outflow from the spring-fed farm pond stabilized at 0.05-0.15 cfs during the summer months.

An analysis of phosphorus data from the two sample periods shows some striking changes. In 1997/98, prior to the alum treatment, the average base flow total P concentration (flows less than 0.15 cfs) was 377.6 ug/l. For all flows exceeding 0.15 cfs the average was 775.5 ug/l indicating a significant amount of P loading from runoff events. In 2008 the average base flow total P concentration fell by 39% to 227.2 ug/l. At higher flows, the change in phosphorus concentration was even more striking. For flows exceeding 0.15 cfs the average total P concentration in 2008 was 127.3 ug/l, an 82% reduction and a reversal of the concentration/ flow relationship (Figure 7).

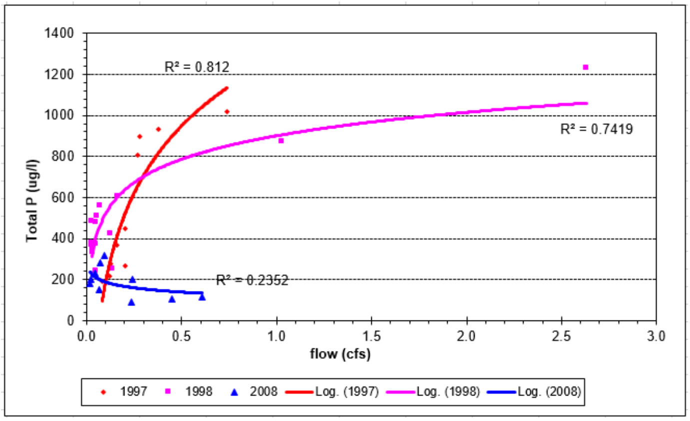

Figure 7. Concentration-flow relationship for the Bass Lake inlet in the 1997/98 and 2008 monitoring periods.

Watershed phosphorus loads for 1998 and 2008 were estimated using the US Army Corps of Engineers $FLUX_{32}$ load estimation software. During the 1998 monitoring period (213 days) the Flux model predicted an annual phosphorus load of 75 kg/y. For the 2008 monitoring period (208 days) the predicted phosphorus load was 20 kg/y, a 73% reduction.

Water quality monitoring between 2010 and 2015 was rather limited, but showed continued recovery. Overall, the disruption of the internal phosphorus loading mechanisms in Bass Lake resulted in nearly 15 years of greatly improve water quality, characterized by clear water and a quality fishery consisting of panfish, largemouth bass, and northern pike.

Alum evaluation study

In 2016 and 2017 the Marinette County LWCD began receiving reports of severe algae blooms and declining water quality in Bass Lake. In response, the LWCD received a WDNR Lake Management Planning Grant in to conduct another round of water quality monitoring and evaluate the fate of the 1999 alum treatment to determine if declining water quality was the result of watershed or internal P loading. The monitoring plan included two years of lake water quality monitoring, stream flow and watershed load monitoring, and evaluating phosphorus release from anaerobic lake sediments. Monitoring data was used to model watershed loading and lake response to external and internal phosphorus loading.

Methods

In 2018 and 2019 lake water quality samples were collected one meter from the surface and one meter from the bottom at the deepest part of the lake according to WDNR monitoring protocols. Samples were analyzed by the Wisconsin State Lab of Hygiene (SLOH) for total P, ortho P, total Kjeldahl nitrogen, nitrate plus nitrite, and ammonia. Chlorophyll-a was measured during the growing season. Dissolved oxygen, temperature, and conductivity were measured in the field at one-meter intervals using a Hydrolab Datasonde 4.

Stream discharge to Bass Lake was measured by continuously monitoring flow through a V-notch weir. Water level above the v-notch was recorded using a Solinst Levelogger LT15/M5 corrected for barometric pressure. Flow through the weir was calculated using the following equation:

$$Q = 2.5 \times H^{2.47}$$

Where H is the vertical distance between the elevation of the lowest part of the weir notch and the elevation of the weir pool

Grab samples were collected from the stream at various flows throughout the monitoring period and analyzed by the Wisconsin SLOH for total P and dissolve reactive phosphorus (ortho P). Watershed loading was calculated using the $FLUX_{32}$ load estimating program developed by the US Army Corps of Engineers and the Minnesota DNR.

Bass Lake sediment cores were collected at two deep-basin locations in Bass Lake (Figure 8) and analyzed by the University of Wisconsin – Stout Center for Limnological Research and Rehabilitation. Three cores were collected at each site for determination of diffusive P flux under anaerobic conditions. A fourth core was collected to examine physical characteristics and sectioned at 1 cm intervals for analysis of aluminum-bound P and mobile P fractions. Detailed sediment analysis methods and results can be found in Appendix A.

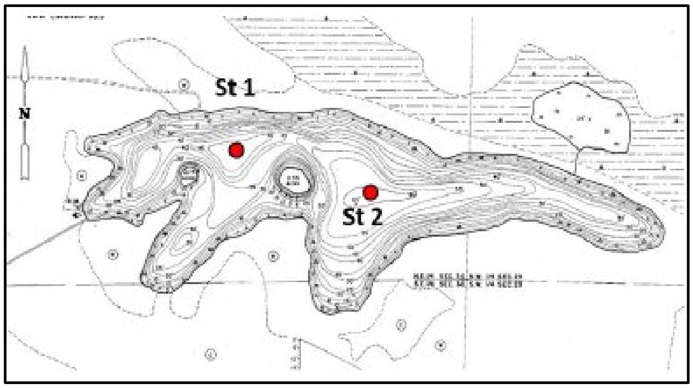

Figure 8. Duplicate sediment samples were collected from the two deep basins in Bass Lake.

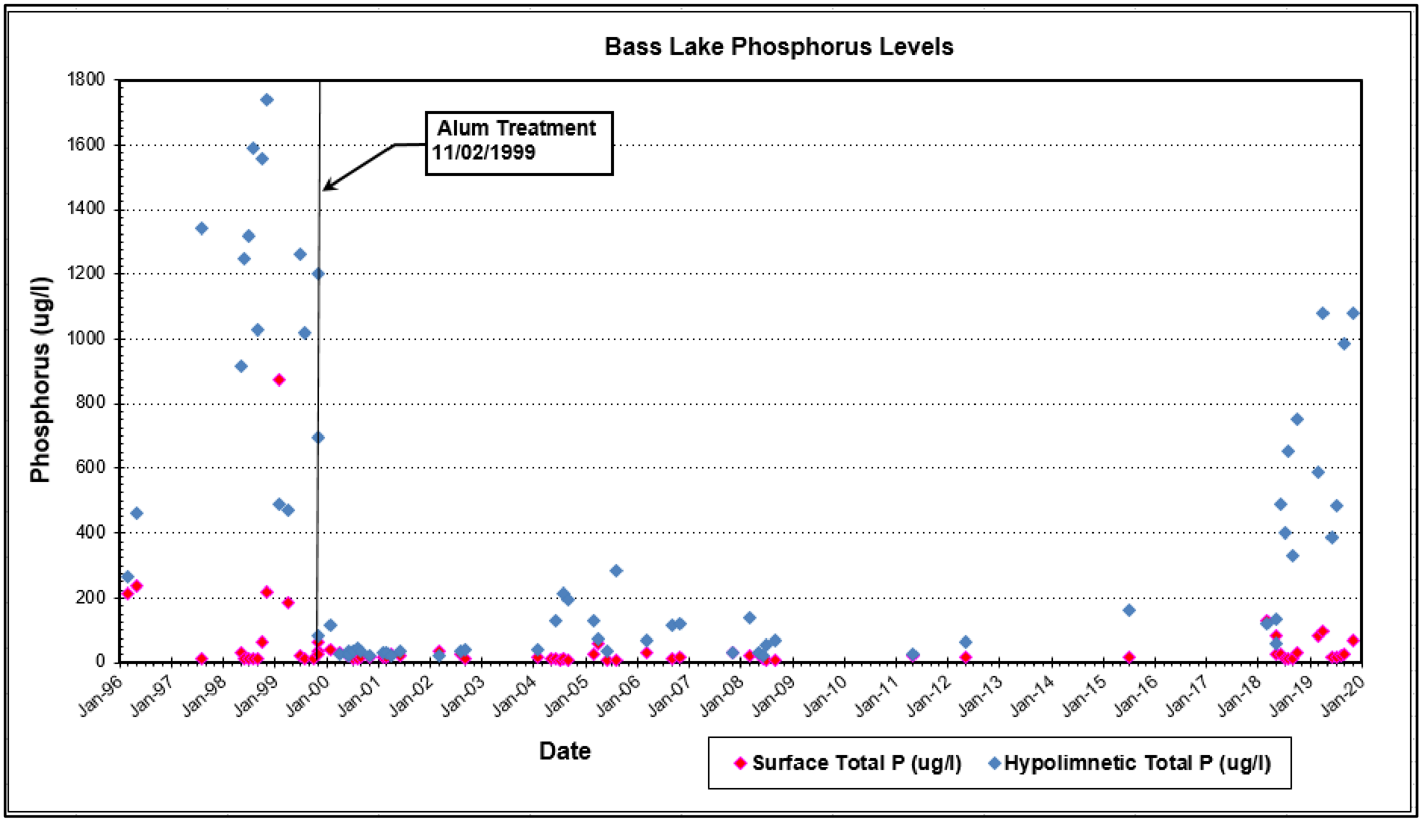

Figure 9. Water quality data clearly shows a drastic reduction in hypolimnetic phosphorus following the 1999 alum treatment. Reports of algae blooms in 2016 and 2017 are linked to a return of nutrient enriched hypolimnetic waters.

Results and Discussion

Prior to the 1999 alum treatment, surface total P in Bass Lake averaged 126.0 ug/l while hypolimnetic total P averaged 664.3 ug/l. In the first 15 years after the alum treatment surface total P averaged just 19.2 ug/l, an 85% reduction (Figure 9). During the same period hypolimnetic P averaged 71.4 ug/l, an 89% reduction. These results clearly show the effectiveness of the alum application and watershed phosphorus controls. However, during the most recent monitoring period, between 2018 and 2020, surface total P averaged 54.9 ug/l, a 218% increase, while hypolimnetic total P averaged 556.0 ug/l, an increase of 679%.

A careful analysis of dissolved oxygen and temperature profiles during monitoring events shows the effect of mixing depth on surface total P levels in Bass Lake. The highest surface total P concentrations were measured in the spring and fall when the thermocline was located deeper in the water column due to mixing, or during winter stratification after a period of deep fall mixing. It should be noted that the depth of the mixed layer during spring and fall turnover was highly variable and complete mixing of the water column was not typical.

Watershed Phosphorus Loading

Discharge to Bass Lake was monitored prior to the alum treatment in 1998-1999, in 2008, and again in 2018-2020. During each monitoring period grab samples were collected from the steam at a variety of flows and the data were used to estimate watershed P loading.

The 2018-2019 flow record was characterized by extreme "flashiness" with frequent peaks and much higher discharge compared to the earlier monitoring periods (Figure 10). The average total P concentration during the period was 390.1 ug/l, which is considerably higher than the average total P concentration measured in 2008 (187.2 ug/l) but not as high as the 1997-98 average (531.4 ug/l).

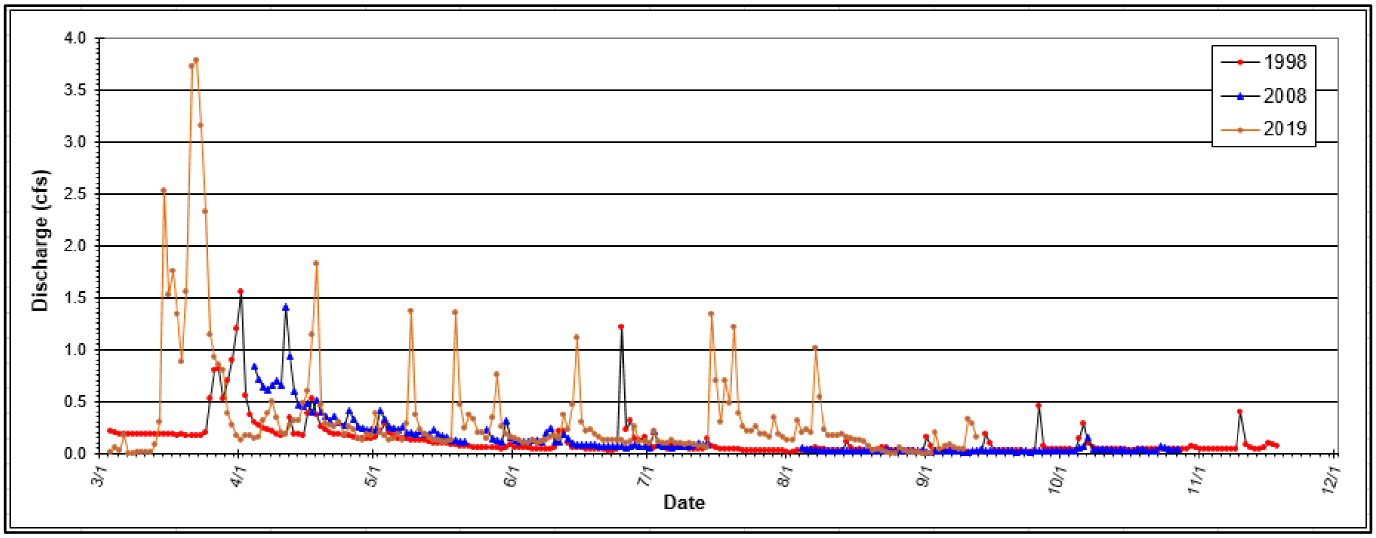

Figure 10. Comparison of patterns of stream discharge during the three monitoring periods. The 2019 flow discharge record shows significantly higher and more numerous peaks in stream flow.

In 1997-98 there was a strong positive relationship between flow and total P (Figure 11). In 2008 the relationship was reversed and there was a negative correlation between flow and Total P, indicating dilution of P levels at higher flows. In 2018-19 the correlation between discharge and total P was again positive but not as strong as it was in 1997-98.

As mentioned, the distribution and severity of runoff events varied greatly between the monitoring periods. 2008 was a dry year with fewer and less intense runoff events. 2018 through 2020 were wet years with numerous runoff events and high flows. Some of the "flashiness" seen in the flow record for the 2018-20 monitoring period may be due to increased impervious surface area in the watershed.

The dairy farm northeast of Bass Lake grew considerably between 1998 and 2020, with a resulting increase in imperious surface area, from 8.6 acres 1998 to 16.7 acres in 2020. Most of the increased area was for feed storage, primarily silage bags and covered silage piles. Runoff from these sites can contain silage leachate, spilled feed, and tracked manure & soil. In 2010 a 2-acre feed storage pad was created and runoff was routed to a small reception tank where the first-flush runoff could be pumped to a manure storage facility. Excess runoff, which is supposedly cleaner, was routed to a vegetated filter strip prior to discharge into a streamside wetland. By 2020 the area dedicated to feed storage expanded to approximately 5.9 acres.

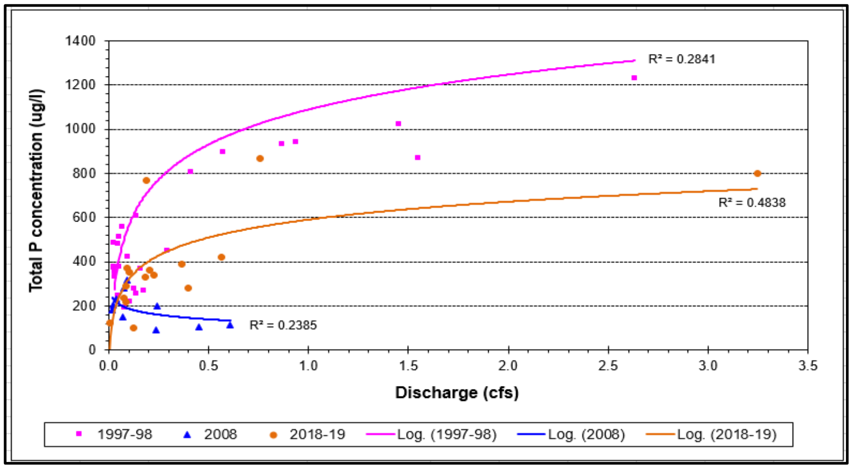

Figure 11. Concentration-flow relationship for the Bass Lake Inlet.

Phosphorus Load Modelling

The FLUX32 Mass Transport Program was again used to evaluate phosphorus loading to Bass Lake based on monitored flows and phosphorus grab samples from the lakes inlet. The loading model predicted a P load of approximately 128 kg/yr during the open water season, significantly higher than 1997-98 (75 kg/yr) or 2008 (20 kg/yr). The increased load can be attributed to a higher runoff volume, and increased phosphorus concentrations in the runoff.

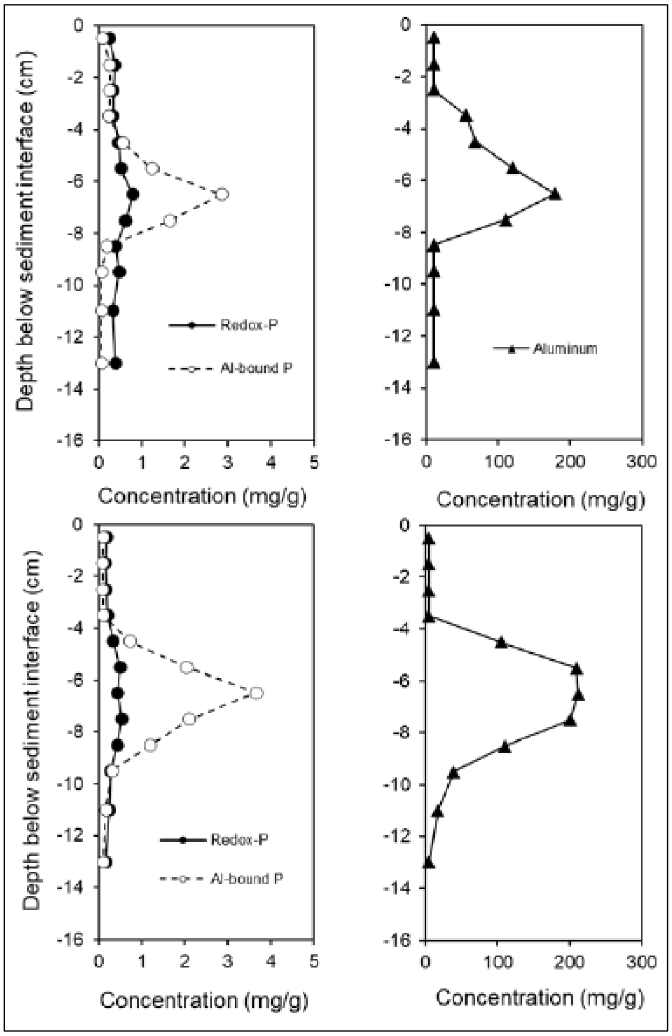

Figure 12. Vertical variations in redox-P, AL-bound P, and extractable aluminum at station 1 (top) and station 2 (bottom).

Sediment P Flux

In each of the six sediment cores the aluminum floc layer was clearly visible approximately 6 cm below the sediment surface. Analysis found that AL-bound P concentrations were highest at 6 cm in conjunction with the floc layer, indicating P became bound to alum over the 19-year period (Figure 12). Aluminum-bound phosphorus declined in concentration to background levels both above and below the 6-cm depth.

Extractable aluminum concentration in the alum floc layer was 126 g/m^2 at station 1 and 178 g/m^2 at station 2, much higher than the targeted 1999 alum dose of 91 g/m^2. This suggests that the AL floc focused after application and became more concentrated in the deep basis (Huser 201, Egemose et al, 2013).

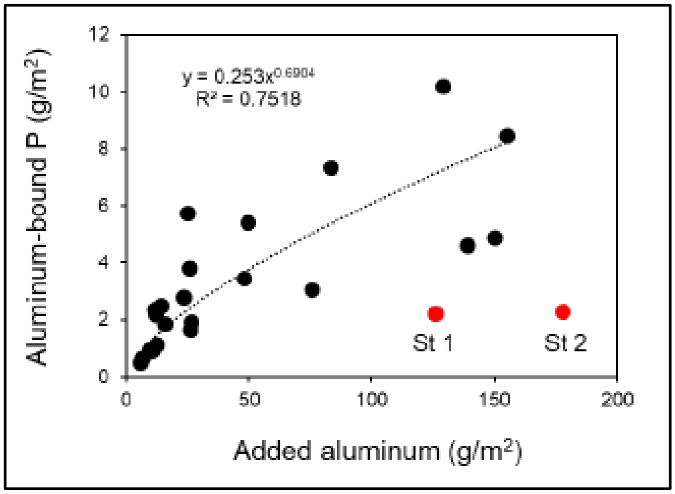

Figure 13. Relationship between aluminum-bound P and added aluminum. Bass Lake is denoted by the solid red circles.

The Al-bound phosphorus concentration in the alum layer was 2.22 g/m^2 at station 1 and 2.27 g/m^2 at station 2. These levels are modest compared to other alum-treated lakes (Figure 13). Indicating that a high AL dose was added relative to the mobile P concentration in the sediment. According to James, 2019 the high AL:P binding ratio might be due to crystallization of the $AL(OH)_3$ floc in the absence of PO_4-P during treatment. Polymerization leads to decreased AL binding sites for P, shortening the longevity of the treatment. Alum overdosing with respect to P concentration can also be cost inefficient.

The concentration of redox-P concentrations in the sediment is the sum of loosely-bound P and iron-bound P. Under anoxic (reduced) conditions this P fraction can be mobilized in the overlying water of the hypolimnion. In Bass Lake the redox-P concentrations in the sediment deposited on top of the alum layer (upper 4 cm of sediment cores) was modest (below the median) compared to other lakes in Minnesota and Western Wisconsin.

Sediment P flux was measured in three replicate cores at each sample site to estimate P loading rates from sediment that has been deposited on top of the

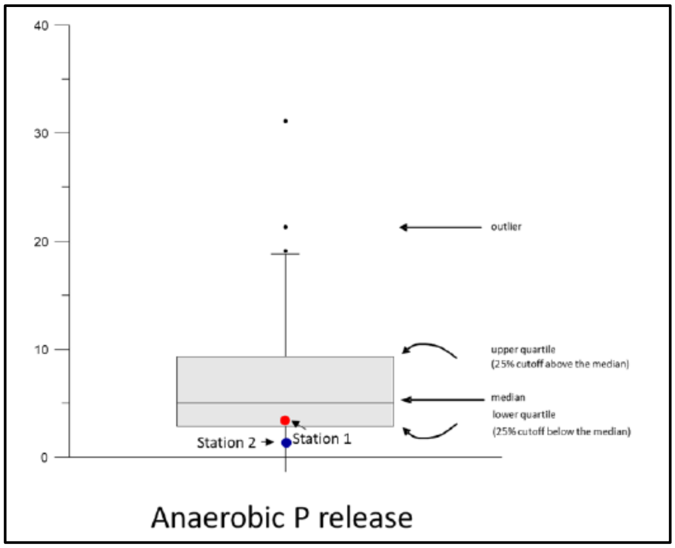

Figure 14. Average rate of P release under anaerobic conditions for Bass Lake sediment cores compared to 50 lakes in east MN and Western Wisconsin.

alum layer over the last 19 years. Mean P release rates under anoxic conditions were 3.41 mg/m^{2}d and 1.93 mg/m^{2}d at stations 1 and 2 respectively. These rates were relatively low compared to those from other lake sediments collected throughout the region (Figure 14). The complete sediment analysis report and discussion can be found in Appendix A.

Conclusions

The 1999 alum treatment resulted in a drastic decline in internal phosphorus release from deep sediments in Bass Lake. This occurred in conjunction with significant reductions in livestock numbers in the Bass Lake watershed and improved phosphorus controls on the one remaining watershed farm. Together, these changes resulted in a dramatic reduction in surface and hypolimnetic total P concentrations and improvements in perceived water quality that persisted for more than 15 years.

Eighteen years after the alum treatment, surface and hypolimnetic total P were once again approaching pre-treatment levels. The reason for the rapid increase appears to be a combination of increased watershed P loading, and internal P loading from sediments deposited on top of the alum floc layer.

A review of land use within the Bass Lake watershed shows that cropland acres have decreased slightly since 1999 while cropping practices have remained largely unchanged. The P export rate from cropland within the watershed should also be reduced since all cropland acres have been managed under nutrient management plans since 2000. Nutrient management plans require all nutrient additions to be completed according to crop needs, restricts the application of animal waste in sensitive areas, and requires manure to be incorporated within 72 hours of application. In practice, manure is typically knifed in or otherwise incorporated immediately after land spreading. Even where allowed, solid pack manure is not winter spread on fields within the Bass Lake watershed.

A more likely source of the increased watershed P loading is runoff from impervious surfaces associated with the farm, particularly the expanded feed storage area. This is supported by the extreme flashiness seen in the 2018-20 flow record. Also, on more than one occasion is was noted that water samples collected from the lake inlet during the fall of 2018 and 2019 smelled like fermenting silage. Runoff from the feed storage area was addressed in the fall of 2022 with the construction of a new runoff collection facility which will hold all runoff from the feed storage area. Contents of the tank will be applied to fields through irrigation or land spreading according to the farms nutrient management plan.

The sediment analysis report (James 2019) concludes that redox-P concentration in surface sediments has rebounded and are currently similar to pre-treatment concentrations, but are still lower than the median for lakes in the region. Despite the moderate rate of sediment P flux, strong thermal stratification, the propensity for incomplete mixing, and the large hypolimnetic volume will likely result in continued episodes of elevated internal P loading during mixing events. As a result, nuisance algae blooms will become more frequent. The resumption of periodic fish kills is also a possibility. Fish kills are most likely after a prolonged period of incomplete mixing that is followed by a rapid and complete turnover just before the formation of ice cover.

As in 1999, improving water quality in Bass Lake can only be accomplished by reducing internal P loading. James (2019) recommends that the target Al concentration of a future alum treatment should be 25–40 g/m^2 to maximize P binding efficiency and improve cost effectiveness. A second alum treatment should also be paired with a continued focus on controlling watershed P loading to extend the longevity of the alum treatment.

References

Egemose SG, Reitzel K, Andersen FØ, Jensen HS. 2013. Resuspension-mediated aluminum and phosphorus distribution in lake sediments after aluminum treatment. Hydrobiologia 701: 79-88.

Huser BJ. 2012. Variability in phosphorus binding by aluminum in alum treated lakes explained by lake morphology and aluminum dose. Wat Res 46:4697-4704.

James, W. 2019. Internal Phosphorus Loading and Sediment Characteristics in Bass Lake, Wisconsin. Laboratory analysis and report. UW Stout Sustainability Sciences Institute – Center for Limnological Research and Rehabilitation.

Kennedy, R.H. and Cooke, G.D. 1982. Control of lake phosphorus with aluminum sulfate: Dose determination and application techniques. American Water Res. Assn., Water Resources Bulletin. 18(3): 389-395.

Rydin, E. and Welch, E.B. 1998. Aluminum dose required to inactivate phosphate in lake sediments. Water Resources, 32, 2969-2976

Internal phosphorus loading and sediment characteristics in Bass Lake, Wisconsin

3 July, 2019

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KEY SUMMARY FINDINGS

1. The 1999 alum floc was located ~ 6 cm below the current sediment surface.
2. The measured concentration of extractable Al was 126 g/m^2 and 178 g/m^2 at stations 1 and 2, much higher than the 1999 target Al dose of 91 g/m^2. This pattern suggested alum floc redistribution and focusing after initial application.
3. Laboratory-derived anaerobic P release rates were a mean 3.41 mg/m^2 d (± 0.64 standard error) at station 1 and 1.93 mg/m^2 d (± 0.25 SE) at station 2. These rates were modest but suggest the occurrence of internal P loading in Bass Lake.
4. Redox-P (i.e., the sum of the loosely-bound and iron-bound P fractions), considered to be functionally importance in internal P loading, were modest in the upper 5-cm of accumulated sediment at 3.91 mg/g and 1.95 mg/g at stations 1 and 2, respectively, but reflect anaerobic P release rates at both stations.

BACKGROUND and OBJECTIVES

Bass Lake, Marinette County Wisconsin, was treated with ~ 61,000 gallons of alum (~91 g/m^2) in early November, 1999, to control internal P loading from anoxic sediments. The objectives of this study were to evaluate the flux of P from anaerobic sediment ~ 19 years later. Specifically,

1. determine diffusive P flux in the laboratory under anaerobic conditions and
2. examine vertical variations in aluminum-bound P (i.e., P bound to the 1999 Al floc), the position of the Al floc in the vertical water column, and mobile P fractions (i.e., iron-bound P) that have settled on top of the Al floc layer over the last 19 y.

Results from this study will be used in conjunction with long-term trends in Bass Lake WQ to evaluate the need for another Al treatment in the future.

METHODS

Field sediment collection

Sediment cores were collected at two stations in Bass Lake in August 2018 for determination of laboratory diffusive P flux from anaerobic sediment and vertical variations in sediment chemistry (Fig. 1). Three replicate cores were collected at each station for determination of diffusive P flux under anaerobic conditions. An additional sediment core was collected at each station for measurement of sediment physical-textural and chemical characteristics. All sediment cores were collected with a gravity corer (Aquatic Research Instruments, Hope ID) equipped with acrylic core liners (6.5 cm inside diameter by 50 cm long). Core liners were stoppered , covered to prevent light exposure, and transported vertically on ice to the laboratory for sectioning and processing within 24 h.

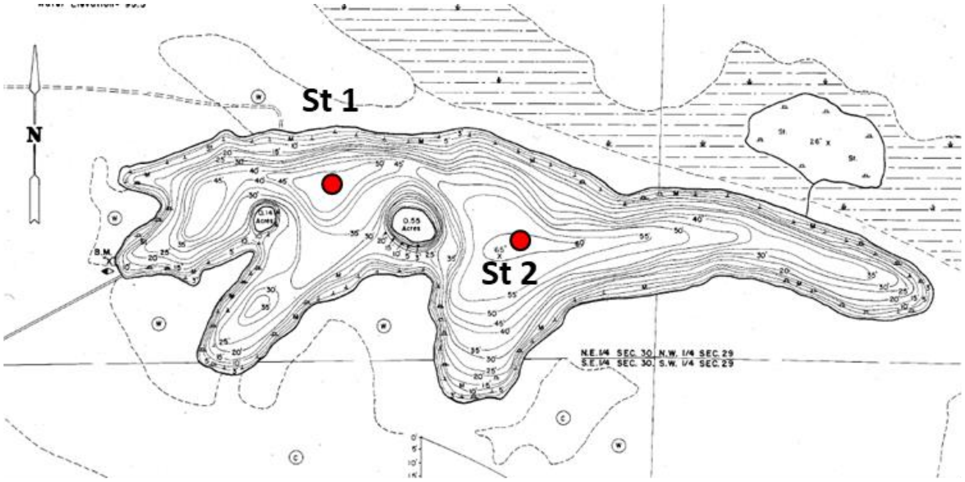

Fig.1. Bass Lake showing station locations for sediment collection

Laboratory-derived rates of P release from sediment

Fig. 2. Sediment core incubation systems for estimation of P release from sediment.

Sediment cores were carefully drained of overlying water in the laboratory and the upper 10 cm of sediment were transferred intact to a smaller acrylic core liner (6.5-cm dia and 20-cm ht) using a core remover tool. Surface water collected from the lake was filtered through a glass fiber filter (Gelman A-E), with 300 mL then siphoned onto the sediment contained in the small acrylic core liner without causing sediment resuspension. They were placed in a darkened environmental chamber and incubated at a constant temperature of ~10 ^{o}C to reflect summer hypolimnetic conditions. The Eh environment in the overlying water was controlled by gently bubbling nitrogen (anaerobic for duplicate cores) through an air stone placed just above the sediment surface in each system. Bubbling action insured complete mixing of the water column but not disrupt the sediment.

Water samples for soluble reactive P were collected from the center of each system using an acid-washed syringe and filtered through a 0.45 µm membrane syringe filter. The water volume removed from each system during sampling was replaced by addition of filtered lake water preadjusted to the proper oxidation-reduction condition. These volumes were accurately measured for determination of dilution effects. Soluble reactive P was measured colorimetrically using the ascorbic acid method (APHA 2011). Rates of P release from the sediment (mg/m^2 d) were calculated as the linear change in mass in the overlying water divided by time (days) and the area (m^2) of the incubation core liner. Regression analysis was used to estimate rates over the linear portion of the data.

Vertical evaluation of sediment P characteristics

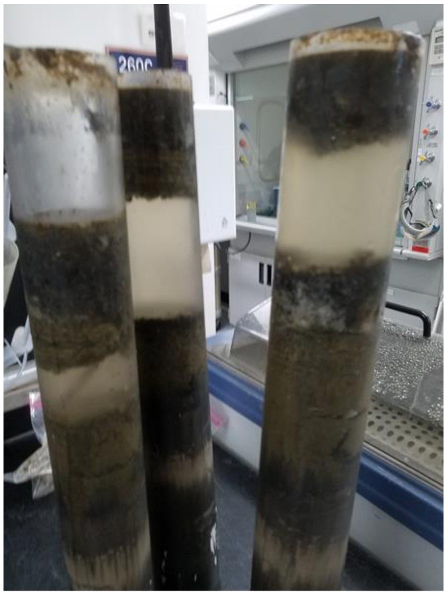

Fig. 3. Sediment core separation within 24 h of collection.

Unfortunately, sediment cores separated overnight in the laboratory, usually near the location of the 1999 Al floc (Fig. 3). Reasons for separation are not known but may have been related to methane production of changes in density after removal from 50-65 ft deep. Water was carefully siphoned from the region of separation to reconsolidate sediments. The sediment cores were then sectioned at 1-cm intervals down to 10 cm and at 2-cm intervals down to 14 cm for analysis of sediment characteristics and P fractions. Sediment sections were analyzed for the variables listed in Table 1. Subsamples were dried at 105 °C to a constant weight and burned at 500 ^{o}C for determination of moisture content, sediment density, and organic matter content (Håkanson and Jensson 2002). Phosphorus fractionation was conducted according to Psenner and Puckso (1988) for the determination of ammonium-chloride-extractable P (1 M NH_4Cl; loosely-bound P), bicarbonate-dithionite-extractable P (0.11 M BD; iron-bound P), and sodium hydroxide-extractable P (1 N NaOH; Aluminum-bound and labile organic P). Aluminum was extracted from sediment with 1 N NaOH and measured colorimetrically after digestion with concentrated nitric and 3.2 M perchloric acid according to Kopáček et al. (2001).

Table 1. Textural-physical variables and mobile sediment phosphorus pools.

Moisture content (%)
Sediment wet and dry bulk density (g/cm^3)
Organic matter content (%)
Loosely-bound P (mg/g)
Iron-bound P (mg/g)
Labile organic P (mg/g)

The loosely-bound and iron-bound P fractions are readily mobilized at the sediment-water interface under anaerobic conditions that result in desorption of P from bacterially-reduced iron compounds (i.e., Fe^{+3} to Fe^{+2}) in the sediment and diffusion into the overlying water column (Mortimer 1971, Boström 1984, Nürnberg 1988). The sum of these fractions are referred to as redox-sensitive P (i.e., redox-P; the P fraction that is active in P release under anaerobic and reducing conditions). In addition, labile organic P (LOP) can be converted to soluble P via bacterial mineralization (Jensen and Andersen 1992) or hydrolysis of bacterial polyphosphates to soluble phosphate under anaerobic conditions (Gächter et al. 1988; Gächter and Meyer 1993; Hupfer et al. 1995). The sum of redox-P and LOP is collectively referred to a biologically-labile P. This fraction is generally active in recycling pathways that result in exchanges of phosphate from the sediment to the overlying water column and potential assimilation by algae.

Results and Discussion

Sediment chemistry

At each station, aluminum-bound P concentrations were maximal at ~ 6-cm below the sediment surface in conjunction with peak concentrations of extractable Al and the location of the Al floc layer, indicating P became to $Al(OH)_3$ over the 19 year period after the 1999 Al application to Bass Lake (Fig. 5). Extractable Al and aluminum-bound

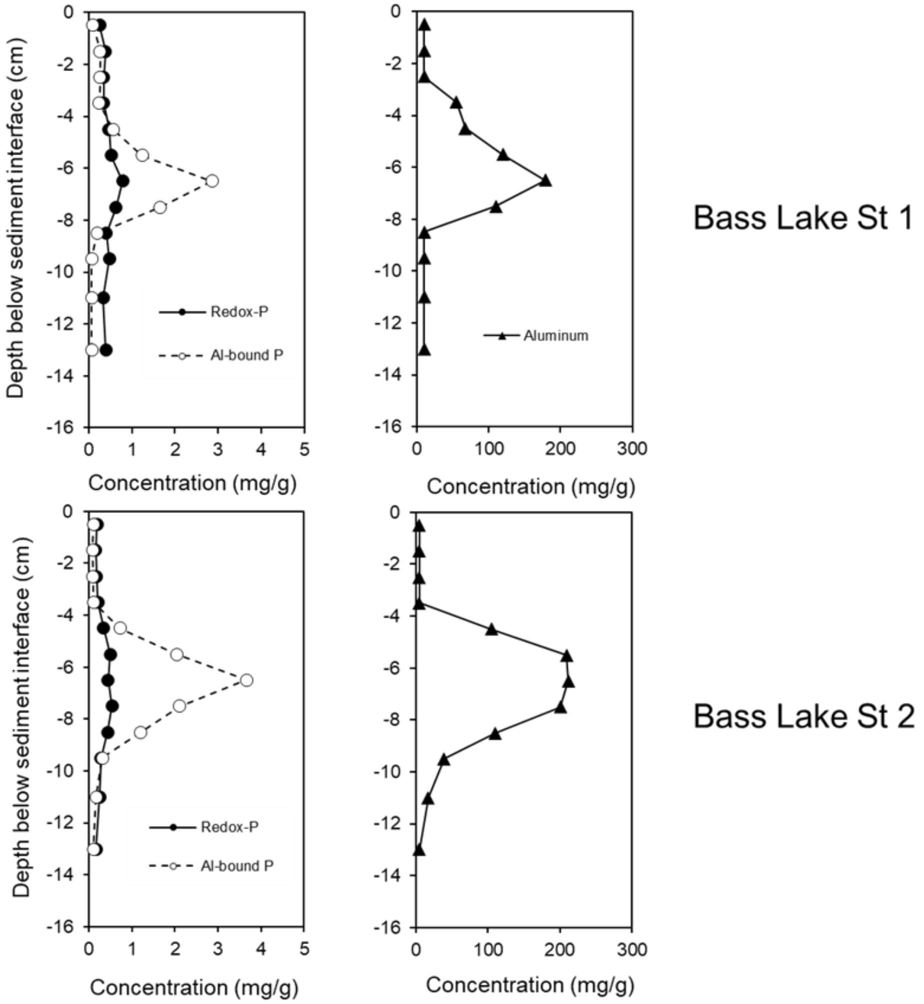

Fig. 5. Vertical variations in redox-P (i.e., the sum of loosely-bound P and iron-bound P), aluminum-bound P (Al-bound P, i.e., P that has been sequestered by the added alum), and extractable aluminum at stations 1 and 2 in Bass Lake.

P declined in concentration to background levels both above and below the 6-cm sediment depth.

The measured extractable Al concentrations in the Al floc layer were 126 g/m^2 at station 1 and 178 g/m^2 at station 2, much higher than the target 1999 Al dose of 91 g/m^2. This pattern suggested that the Al floc focused after application and became more concentrated in the deep basin (Huser 2012, Egemose et al. 2013). In contrast, the concentration of P bound by the Al floc in Bass Lake (station 1 = 2.22 g/m^2, station 2 = 2.268 g/m^2) was modest compared to other Al-treated lakes (Fig. 6). This pattern suggested that a high Al dose was added relative to the mobile P in the sediment. The Al:P binding ratio (i.e., the mass of Al required to bind 1 part P mass) in Bass Lake sediment was ~ 68:1 mass, which was high compared to other Al-treated lakes in Washington state (~ 11:1, Rydin et al. 2000) and Denmark (~ 13:1, Egemose et al. 2013).

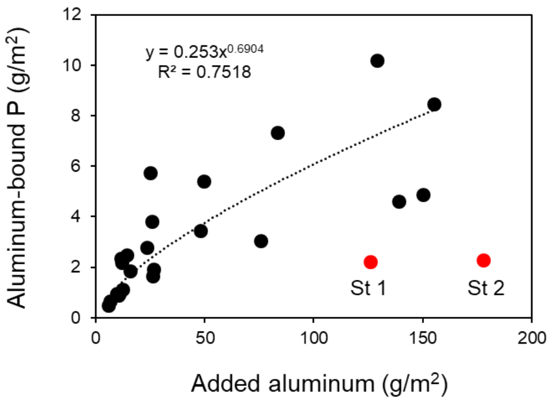

Fig. 6. Relationship between aluminum-bound phosphorus (P) and added aluminum. Bass Lake is denoted by the solid red circle.

A higher Al:P binding ratio for Bass Lake sediments might be due to crystallization of the $Al(OH)_3$ floc in the absence of PO_4-P during treatment. For instance, de Vicente et al. (2008) found that Al binding efficiency for P can decrease by up to 75% within a short period of time (< 3 m) if not exposed to P, due to polymerization into a more ordered crystalline structure. Polymerization leads to decreased Al binding sites for P, shortened longevity, and a higher mass of Al needed to bind PO_4-P (i.e., higher Al:P binding ratio). In addition, Al overdosing with respect to available P can be cost inefficient (de Vicente et al. 2008).

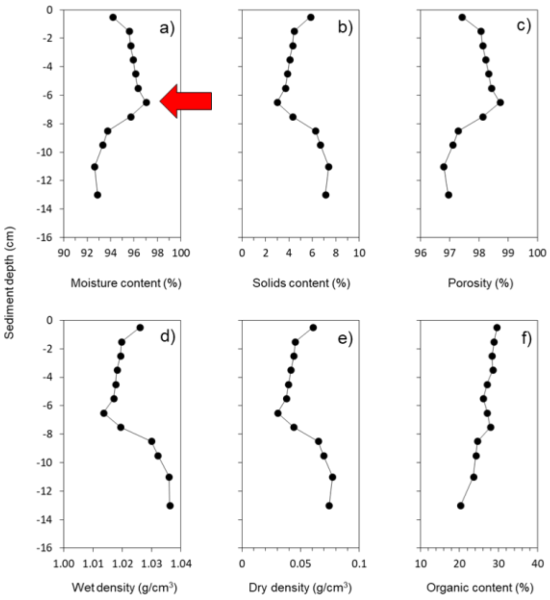

Fig. 7. Vertical variations in a) moisture content, b) solids content, c) porosity (i.e., interstitial or porewater volume), d) wet bulk density, e) dry bulk density, and f) organic matter content for station 1 sediments, Bass Lake. Red arrow denotes approximate location of the Al floc.

An example of vertical variations in sediment physical and textural characteristics is shown for station 1 sediments in Figure 7. In general, moisture content was high and increased to a peak in the vicinity of the Al floc layer. Density exhibited the opposite pattern; it was lowest in the vicinity of the Al floc layer. This pattern may be an artifact of sediment core separation and failure to completely reconsolidate the two sediment layers. Alternatively, the Al floc has very low wet and dry density after formation and typically settles on top of the sediment surface rather than sinking or mixing into deeper layers after application (James 2017). New sediment depositing on top of the Al floc layer over a 19-y period was slightly denser, leading to the inverted moisture and density vertical profiles at the ~ 6-cm depth.

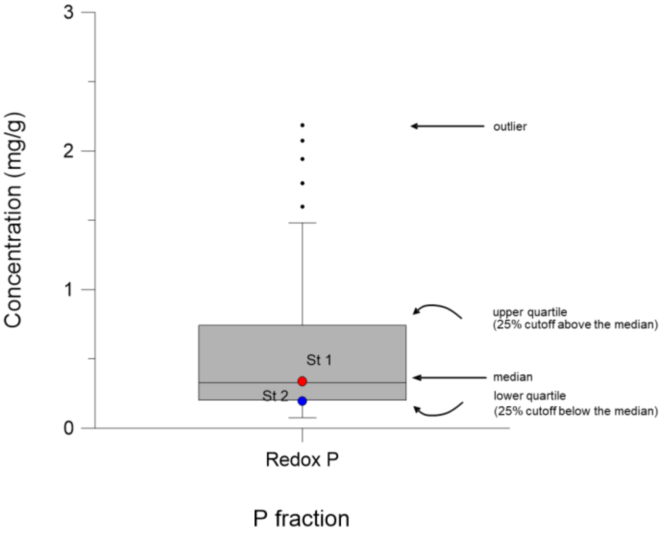

Fig. 8. Box and Whisker graph showing redox-P concentrations in the surface sediment of Bass Lake compared to ~ 50 lakes in the east MN-west WI region.

After 19 y of sediment deposition and burial of the Al floc layer, surface redox-P (i.e., the sum of loosely-bound P and iron-bound P) concentrations have rebounded and reflect pre alum treatment conditions (Fig. 5). Redox-P concentrations in the upper ~ 4 cm sediment were modest compared to other lakes in Minnesota-western Wisconsin, falling near the median at station 1 and the lower 25% quartile for station 2 (Fig. 8).

Sediment phosphorus flux

Soluble P concentrations increased in the overlying water column of laboratory sediment incubation systems under anaerobic or anoxic (i.e., devoid of dissolved oxygen) conditions (Fig. 9). Rates of P release from anaerobic sediment were 3.41 (±0.64 standard error) and 1.93 mg/m^2 d (± 0.25 SE) at station 1 and 2, respectively (Table 2). These rates were relatively low compared to rates measured from other lake sediment collected throughout the region (Fig. 10). Overall, rates fell within or below the 25% quartile.

Table 2. Mean rates of phosphorus release (diffusive P flux) under anaerobic conditions for Bass Lake sediment..

Location	Rate (mg/m^2 d)	Standard error
St 1	3.41	0.64
St 2	1.93	0.25

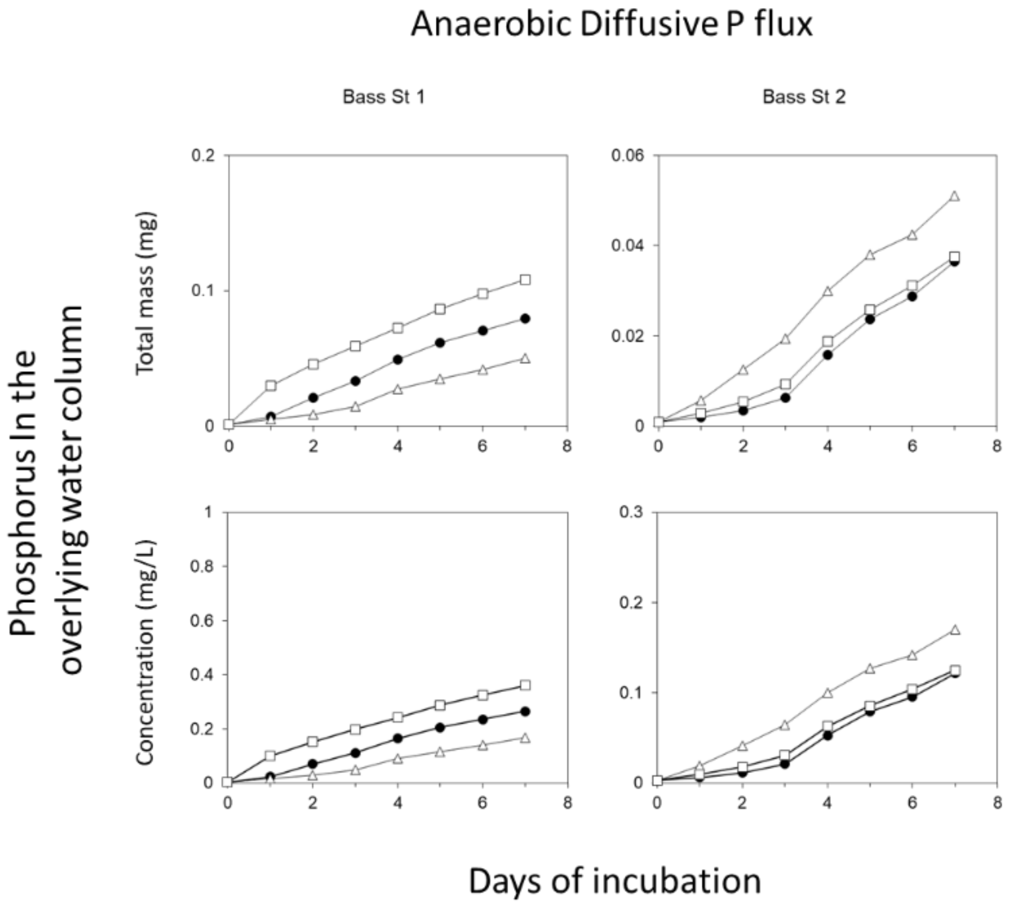

Fig. 9. Changes in soluble phosphorus mass and concentration in the overlying water column of intact sediment cores collected from Bass Lake and incubated at ~ 10 C under anaerobic conditions.

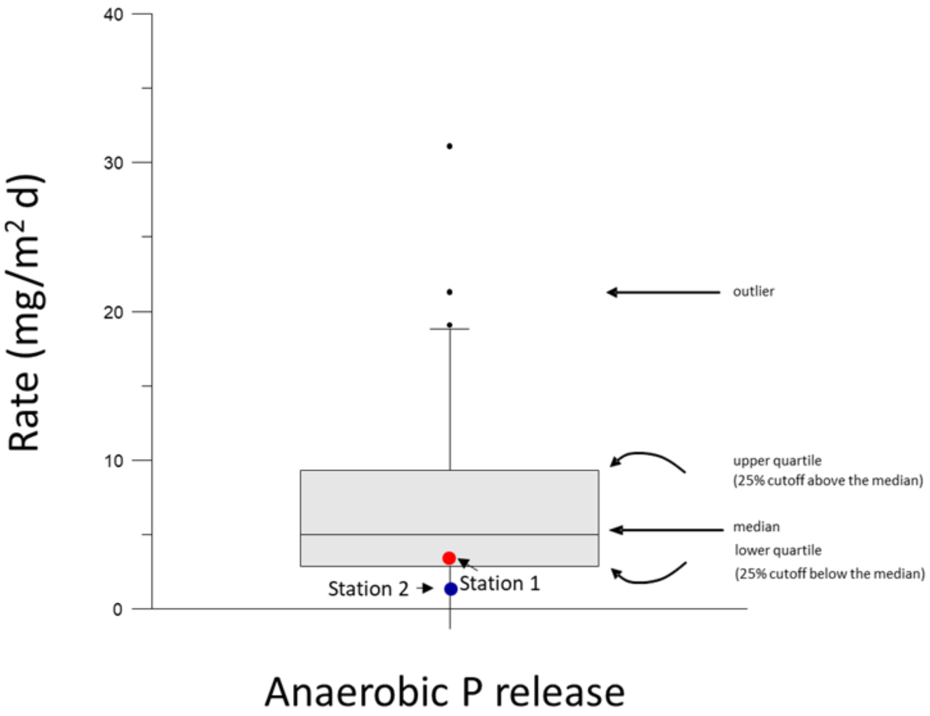

Fig. 10. Box and Whisker graph showing rates of P release under anaerobic conditions for sediment cores collected in Bass Lake compared to ~ 50 lakes in the east MN-west WI region.

CONCLUSIONS

Bass Lake profundal sediments were treated with a ~ 91 g/m^2 alum application in 1999. Nineteen years later (2018), the alum floc layer has become buried with ~ 6 cm of sediment at stations 1 and 2. Redox-P (i.e., sediment P that has been correlated to internal P loading) concentrations are currently moderate in the surface sediments and similar to pretreatment concentrations. Laboratory-derived rates of P release from sediment under anaerobic conditions are moderate at 1.9 to 3.4 mg/m^2 d. Since Bass Lake exhibits summer anoxia, accumulation of soluble P in hypolimnion may now be contributing to algal blooms. Upward transport of hypolimnetic P to the epilimnion can occur via mixing and entrainment or direct access by motile algal species (Barbiero and Welch 1992, Barbiero and Kann 1994, Istvanovics et al. 1993, 2000, Perakis et al. 1996, Pettersson et al. 1993).

Future Al treatment should consider application of lower Al concentrations of 25-40 g/m^2 during hypolimnetic anoxia and the buildup of hypolimnetic P. Lower Al doses will maximize P binding efficiency (i.e., improve cost-effectiveness) and application during periods of hypolimnetic P accumulation will result in some immediate P binding of internal loads while reducing Al crystallization. Lower Al dose applications can also be conducted over multiple years (i.e., year 1, year 4, year 7 or year 1, year 3, year 5, etc) to both maximize P binding and control internal P loading for decades (Huser et al. 2016).

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REFERENCES.

APHA (American Public Health Association). 2011. Standard Methods for the Examination of Water and Wastewater. 22th ed. American Public Health Association, American Water Works Association, Water Environment Federation.

Barbiero RP, Welch EB. 1992. Contribution of benthic blue-green algal recruitment to lake populations and phosphorus translocation. Freshwat Biol 27:249–260.

Barbiero RP, Kann J. 1994. The importance of benthic recruitment to the population development of *Aphanizomenon flos-aquae* and internal loading in a shallow lake. J Plankton Res 16:1581–1588.

Boström B, Jansson M, Forsberg C. 1982. Phosphorus release from lake sediments. Archiv Hydrobiol–Beih Erge Limnol 18:5-59.

Boström B. 1984. Potential mobility of phosphorus in different types of lake sediment. Internat Rev Hydrobiol *69:* 457–474.

Egemose SG, Reitzel K, Andersen FØ, Jensen HS. 2013. Resuspension-mediated aluminum and phosphorus distribution in lake sediments after aluminum treatment. Hydrobiologia 701: 79-88.

Gächter R., Meyer JS, Mares A. 1988. Contribution of bacteria to release and fixation of phosphorus in lake sediments. Limnol. Oceanogr 33:1542-1558.

Gächter R, Meyer JS. 1993. The role of microorganisms in mobilization and fixation of phosphorus in sediments. Hydrobiologia 253:103-121.

Håkanson L, Jansson M. 2002. Principles of lake sedimentology. The Blackburn Press, Caldwell, NJ USA.

Hupfer M, Gächter R., Giovanoli R. 1995. Transformation of phosphorus species in settling seston and during early sediment diagenesis. Aquat Sci 57:305-324.

Huser BJ. 2012. Variability in phosphorus binding by aluminum in alum treated lakes explained by lake morphology and aluminum dose. Wat Res 46:4697-4704.

Huser BJ et al. 2016. Longevity and effectiveness of aluminum addition to reduce sediment phosphorus release and restore lake water quality. Wat Res 97:122-132.

Istvanovics V, Pettersson K, Rodrigo MA, Pierson D, Padisak J, Colom W. 1993. *Gloeotrichia echinulata*, a colonial cyanobacterium with a unique phosphorus uptake and life strategy. J Plankton Res 15:531–552.

Istvanovics V, Shafik HM, Presing M, Juhos S. 2000. Growth and phosphate uptake kinetics of the cyanobacterium, *Cylindrospermopsis raciborskii* (Cyanophyceae) in throughflow cultures. Freshwat Biol 43:257–275.

Mortimer CH. 1971. Chemical exchanges between sediments and water in the Great Lakes – Speculations on probable regulatory mechanisms. *Limnol Oceanogr* 16:387-404.

Nürnberg GK. 1988. Prediction of phosphorus release rates from total and reductant-soluble phosphorus in anoxic lake sediments. *Can J Fish Aquat Sci* 45:453-462.

Perakis SS, Welch EB, Jacoby JM. 1996. Sediment-to-water blue-green algal recruitment in response to alum and environmental factors. Hydrobiologia 318:165–177.

Pettersson K, Herlitz E, Istvanovics V. 1993. The role of *Gloeotrichia echinulata* in the transfer of phosphorus from sediments to water in Lake Erken. Hydrobiologia 253:123–129.

Psenner R, Puckso R. 1988. Phosphorus fractionation: Advantages and limits of the method for the study of sediment P origins and interactions. Arch Hydrobiol Biel Erg Limnol 30:43-59.